Sulfuric Acid Monohydrate: Formation and Heterogeneous Chemistry in the Stratosphere

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Abstract

We have investigated some thermodynamic properties (i.e. freezing/nlcdting points) and heterogeneous chemistry of sulfuric acid monohydrate (SAM, $H_2SO_4 \cdot H_2O$), using a fast flow-reactor coupled to a quadrupole mass spectrometer. The freezing point observations show that for sulfuric acid contents between 75 and 85 wt % the monohydrate crystallizes readily at temperatures between 220 and 240 K. Once formed, SAM can be thermodynamically stable in the H_2O partial pressure range of (1 -4)x1 0"^{4} Torr and in the temperature range of 220-240 K. For a given H_2O partial pressure, SAM melts at lower temperatures. The reaction probability measurements indicate that the hydrolysis of N_2O_5 is significantly suppressed duc to the formation of crystalline SAM: the reaction probability on water-rich SAM is on the order of 10^{-3} at 210 K and decreases by more than an order of magnitude for the acid-rich form. The hydrolysis rate of $ClONO_2$ on water-rich SAM is even smaller, on the order of 10-4 at 195 K. No enhancement of these reactions is observed in the presence of 1 ICl vapor at the stratospheric concentrations, in addition, BET analysis of gas-adsorption isotherms has been performed to characterize the surface roughness and porosities of the SAM substrates. The results suggest the possible formation of SAM in some regions of mid- or low latitude stratosphere and, consequently, much slower heterogeneous reactions on these frozen aerosols.

Introduction

It is now well recognized that the high rates of Antarctic ozone destruction arc induced by surface-catalyzed reactions on polar stratospheric cloud (PSC) particles [Solomon, 1988]. The heterogeneous reactions of primary interest in the stratosphere arc as follows,

$$ClONO_2 + H_2O \rightarrow HOCl + HNO_3 \quad (1)$$

$$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3 \quad (2)$$

$$HOCl + HCl \rightarrow Cl_2 + H_2O \quad (3)$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \quad (4)$$

$$N_2O_5 + HCl \rightarrow ClNO_2 + HNO_3 \quad (5)$$

These reactions transform stable chlorine reservoir compounds into photochemically active forms which arc rapidly converted into the chlorine radicals (Cl and Cl O), leading to catalytic ozone destruction, Of equal importance to the polar stratospheric ozone depletion is the concomitant repartitioning of nitrogen species ($NO_,$) from the gas phase to the condensed phase (in the form of NO_y) since they can be removed irreversibly from the stratosphere due to gravitational sedimentation of PSC particles, If significant HNO_3 remains in the polar spring, the chlorine radicals will be converted back to $ClONO_2$ by the reaction of ClO and NO_2 produced from HNO_3 photo] ysis, halting ozone depletion,

The PSC particles which act as catalysts for the heterogeneous reactions arc generally classified as nitric acid trihydrates (type I) and water-ice (type II) [Crutzen and Arnold, 1986; Toon et al,, 1986], Laboratory studies have demonstrated that the heterogeneous reactions proceed readily on the proposed PSC materials [DeMore et al., 1992; Kolb et al., 1994], Also, the occurrence of heterogeneous reactions on particles in the polar regions during winter and early spring has been clearly seen in field observations, showing chemical changes such as the increase in C1O and concurrent decreases in I] Cl, $ClONO_2$, and ozone as measured from inside to outside of the chemically perturbed regions in Antarctica and the Arctic [Anderson et al., 1991; Brune et al.,1991; Webster et al., 1993].

Sulfate aerosols in the stratosphere have also been proposed to affect the balance of global ozone via heterogeneous reactions analogous to those implicated in polar ozone loss [Hofmann and Solomon, 1988; Brasseur et al., 1991 ; Rodriguez et al., 1991]. The sulfate aerosol layer,

which exists at latitudes between 10 and 30 km, is composed of sulfuric acid particles with a mean diameter of about 0.1 pm and concentration from 1 to 10 cm^{-3} under unperturbated stratospheric conditions, Major volcanic eruptions, such as that of Mt. Pinatubo, may significantly increase the particle size and concentration, Steele and Hamill [1981] first estimated the sulfate aerosol compositions as a function of temperature, predicting aerosol compositions of 70-80 wt % at mid-latitudes and of less than 50 wt % at high latitudes. The global distribution and seasonal variation of the acidity of stratospheric aerosols have been recently compiled by Yue et al. [1994], on the basis of temperature and water partial pressure data obtained by the Stratospheric Aerosol and Gas Experiment 11 (SAGE 11),

1 lowever, the detailed composition and phase of stratospheric sulfate aerosols have not been firmly established, Present knowledge of phase properties and composition of these aerosols is only inferred indirectly from field observations [Dye et al., 1992; Pueschel et al., 1992; Browell et al., 1993; Rosen et al., 1993; Rinsland et al., 1994]. Also, theoretical predictions of freezing points of sulfate aerosols at stratosphere ic conditions are severely limited by the lack of fundamental physical parameters concerning surface energies of various sulfuric acid hydrates [Jensen et al., 1991; Luo et al., 1993]. Recently, a number of studies have investigated freezing points of liquid sulfuric. acid using bulk solutions [Middlebrook et al., 1993; Ohtake, 1993; Zhang et al., 1993; Beyer et al., 1994; Song, 1994]: many of the studies dealt with rather dilute sulfuric acid, in terms of relevance to PSC formation, For example, crystalline sulfuric acid hydrates such as tetrahydrate and hemihexahydrate [Middlebrook et al., 1993; Zhang et al., 1993] have been proposed to form and persist in certain stratospheric regions.

Both the phase and composition of sulfate aerosols arc likely to affect their ability to promote heterogeneous reactions. In the laboratory, the reaction probabilities of reactions] to 3 on liquid sulfuric acid have been shown to depend strongly on the acid content: they proceed efficiently in dilute sulfuric acid solutions at low temperatures [Molina et al., 1993; Hanson and Ravishankara, 1994; Zhang et al., 1994a], Hence, these reactions occurring on stratospheric sulfate aerosols at high latitudes in winter and early spring could provide important pathways for chlorine activation, Outside of the polar regions, the most significant heterogeneous reaction on the sulfate aerosols is believed to be the hydrolysis of N_2O_5 (reaction 4) with the consequent changes in the abundance of various nitrogen and chlorine species, Hanson and Ravishankara

[1993] have recently determined that the reaction probability for N_2O_5 hydrolysis on crystalline sulfuric acid tetrahydrate (SAT, or a composition of 57,6 wt%) is quite different from that on the liquid surfaces,

Apparently, in addition to study ing chemical reactivity of various sulfuric acid hydrates, laboratory investigation of conditions necessary to cause freezing of the supercooled sulfuric acid is also needed. Furthermore, experimental determination of the melting behavior of various sulfuric acid hydrates is important to predicting their stability regions in the stratosphere.

in this work, wc investigate sulfuric acid films that simulate stratospheric sulfate aerosols, using a flow tube coupled to a mass spectrometer. We describe freezing point observations of liquid sulfuric acid films at the stratospheric temperatures (1 90-240 K) and water partial pressures (1 -4x 10-4 '1'err), focusing on concentrated sulfuric acid solutions and possible formation of sulfuric acid monohydrate (SAM, or a composition of 84,5 wt O/O). We also report results of experiments designed to examine melting of SAM films under stratospheric conditions. in addition, BET analysis of gas-adsorption isotherms is performed to characterize the surface roughness and porosities of both SAM and SAT substrates, Finally, reaction probabilities involving N_2O_5 and $ClONO_2$ with H_2O and HCl on SAM films arc measured and implications for the stratosphere arc discussed.

Experimental Section

Measurements of freezing/melting points and reaction probabilities were performed in a horizontally mounted flow reactor (2.8-cm i.d.) in conj unction with a mass spectrometer. The detection scheme utilized both electron impact (EI MS) and chemical ionization (CIMS) mass spectrometry. The majority of the data was taken using EI h4S: the experimental apparatus and procedures were nearl y identical to those described by us in a separate publication [Zhang et al,, 1994a]. The detailed description about the CIMS apparatus has been given by Leu et al. [1994]. Briefly, the CIMS consisted of an ion flow tube through which a large flow of helium at a pressure of about 0.2 Torr was maintained and where the ion-molecule reactions occurred. The reactant ions, 1" or SF_6^-, were produced in the ion ftow tube by electron attachment to CF_3I or SF_6. I' ions were used to selectively detect N_2O_5 and $ClONO_2$ in the presence of HNO_3 since 1'

reacts readily with N_2O_5 and $ClONO_2$ to produce NO_3^- (62 amu) but not with HNO_3. At very high HNO_3 concentrations ($>10^{11}$ molecules cm^{-3}), some production of NO_3^- was also detected due to $I^- + HNO_3$ reaction with I-. By using the relative concentrations of I^- and HNO_3 along with the characteristic reaction time in our system, we estimated a rate coefficient consistent with that suggested by Fehsenfeld et al. [1975]. SF_6^- reacts with N_2O_5, $ClONO_2$, and HNO_3, yielding NO_3^-, $F^- \cdot ClONO_2$ (116 amu), and $NO_3^- \cdot HF$ (82 amu). Detection sensitivities for these species were approximately 10^7-10^8 molecules cm^{-3} in the neutral flow tube. Depending on the experimental needs, one of the reactant ions, I^- or SF_6^-, was employed.

The flow tube was surrounded by an inner jacket in which refrigerated methanol was circulated. The outer jacket of the flow tubes was evacuated to provide thermal insulation. Three movable injectors were located at the upstream end of the flow tube. A heated injector (1.0-cm o.d.) was used to add H_2O (this injector was normally positioned near the upstream end to prevent possible warming of the substrate). The reactants (such as $ClONO_2$ or N_2O_5) were introduced through a centrally-located unjacketed injector (0.3-cm o.d.), and a third injector of similar o.d. was used to introduce other trace species such as HCl. All the gaseous species were delivered to the flow tube along with small He flows (0.1-5.0 cm^3 min^{-1} at STP) and further diluted in the main He flow (280 cm^3 min^{-1} at STP) before contacting the sulfuric acid surface. Typically, the flow tube was operated at a total pressure of 0.5 Torr and about 890 cm s^{-1} flow velocity.

Liquid H_2SO_4 films were prepared by totally covering the inside walls of the flow tube with sulfuric acid solutions. The thickness of the films was estimated to be about ~ 0.1 mm. To determine the H_2SO_4 content of the liquid films, we used the temperature and H_2O partial pressure to convert the H_2SO_4 wt %, according to the vapor pressure data of Zeleznik [1991] and Zhang et al. [1993]. The error limit in estimating the H_2SO_4 content of the films was about 1-2 wt %, considering uncertainties associated with the temperature and water vapor pressure. Crystallization of the liquid coating can be distinguished visually due to its opaqueness and well-defined crystal structures, as opposite to the liquid state indicated by the clearness and transparency. A photography of the crystalline SAM film formed in the flow tube is shown in Figure 1. Rough surfaces and grain boundaries are clearly evident in this figure, suggesting SAM surface areas should be in general greater than the geometric area of the flow reactor, to be

discussed later. The SAM surfaces were verified to melt within a degree of the pure SAM Inciting point [Gable et al., 1 950], The temperature and water partial pressure in the flow tube jointly quantified the thermodynamic state of the SAM surfaces [Molina, 1994]: the H_2SO_4-rich and 1 I_2O-rich forms could be generated by controlling the equilibrium 1 I_2O vapor pressure through addition or evaporation of small amounts of water at a constant temperature or by controlling the temperature at a constant 1 I_2O partial pressure,

Reaction probabilities (γ) were calculated from first-order rate constants (k) corresponding to the reactant loss or product growth:

$$\gamma = 2rk/(\omega + t\text{-}k) \quad (6)$$

where r is the radius of the flow tube and ω is the mean thermal velocity of the reactant. To account for the reactant radial and axial gradients in the flow tube which arose when there was a large reactant wall loss, the observed fllst-order rate constants (k_{obs}) were corrected for gas diffusion by the method suggested by Brown [1978] to obtain k. The $ClONO_2$ and N_2O_5 diffusion coefficients in helium used in the Brown calculations were 176 and 171 cm^2/s at 200 K and 1 '1'err, both with a temperature dependency of $T^{1.76}$ [Marrero and Mason, 1972]. These corrections were approximately 10% for small γ values ($\gamma < 0.01$), and as large as a factor of 4 for large γs ($\gamma > 0.2$).

The experimental approach for studying surface roughness and porosities of crystalline SAM and SAT was similar to that previously described by Gregg and Sing [1982] and Keyser and Leu [1993]. Briefly, surface area measurements employed the Brunauer, Emmett, and Teller (BET) method to analyze krypton (Kr) adsorption isotherms obtained at 77.2 K. Liquid sulfuric acid films (57.7 and 84.5 wt% for SAT and SAM, respectively) were prepared at the bottom of a glass adsorption cell with a geometric area of 45 cm^2 and frozen at low temperatures. The adsorption cell was then submerged in liquid nitrogen and the isotherms were determined volumetrically by expanding Kr from a calibrated volume at room temperature.

Results and Discussion

Freezing Point Measurements

We have investigated the supercooling behavior and freezing points of sulfuric acid films using the flow tube/mass spectrometer apparatus. The measurements were carried out by slowly cooling a liquid sulfuric acid film (with an initial H_2SO_4 content between 60 and 85 wt%) at less than 0.1 K rei"-'. Upon exhibiting some crystallization, the sample was then held at the constant temperature until completely frozen. A kcy aspect of the experiment was the maintenance of a constant water partial pressure during freezing. Typically, the crystalline growth was initially quite pronounced and slowly propagated throughout the coating,

Figure 2 depicts tbc observed freezing temperatures along with the H_2SO_4 wt % derived from the H_2O partial pressure and temperature in the flow tube, The equilibrium freezing points of sulfuric acid [Gable et al., 1950] arc plotted as the solid curves. The smooth dashed curves represent deliquescence of sulfate aerosols at various stratospheric H_2O mixing ratios [Steele and Hamill, 1981]. Also shown in this figure as the dotted line a-b is the extension of liquid/SAM coexistence curve delineating the SAM stability regime. Figure 2 shows that the observed freezing temperatures depend markedly on the H_2SO_4 content, For acid contents between 75 and 85 wt %, the films froze at temperatures between 220 and 2,S0 K; a freezing point maximum occurred for about 85 wt % H_2SO_4. In contrast, dilute sulfuric acid supercooled readily. The films with acid contents between 60 and 75 wt %, as labeled by the horizontal bar, did not freeze, even after being held at 190 K for hours.

In nearly all experiments, wc observed that, if the sulfuric acid films froze at temperature and water partial pressures commonly found in the mid- and low latitude stratosphere, SAM was the predominant hydrate. The identity of the frozen substrates was unambiguously confirmed by examining the melting points of the substrates, which matched the literature value of SAM melting point within a degree [Gable et al., 1950], It is also important to note that tbc freezing process in the our experiments should resemble that occurring in the stratosphere. Additionally, because equilibrium between the condensed and gas phases is actively maintained for sulfate aerosols in the stratosphere, a partially frozen mixture is implausible, If a portion of an 80 wt % acid aerosol droplet freezes to form SAM, for example, the remaining liquid would become more dilute. Subsequently, some of the water in the droplet would evaporate to maintain the constant water partial pressure, '1'bus, the solid part will continuously grow in such a manner until crystallization is complete.

The extensive supercooling for 60-75 wt ?40 H_2SO_4 is consistent with that reported previously [Middlebrook et al., 1993; Ohtake, 1993; Zhang et al., 1993; Beyer et al., 1994; Song, 1 994], Freezing points of more concentrated sulfuric. acid (> 75 wt ?'0) have been investigated by Ohtake [1992] and Song [1 994] using bulk solutions. While our results arc qualitatively similar to those by Song [1994], who also observed a freezing point maximum around the pure SAM composition, this latter study yielded freezing temperatures about 20-30 K lower than the present values for H_2SO_4 contents between 75 and 85 wt o/.. 'l'he work of Ohtake [1992.] apparently missed this freezing point maximum, presumably due to sparse data collected in this composition range. Both these studies investigated 1 I_2SO_4 supercooling in caped test tubes, which may represent non-equilibrium processes. in fact, SAM growth from a solution less than 84.5 wt O/. could be hindered in a closed system, even if nucleation has been initiated. This occurs because partial freezing of the solution causes a shift in the acid content of the remaining liquid, leading to a more dilute solution. As a result, further growth of SAM can be inhibited, when evaporation of excess H_2O is not possible. An analogue phenomenon has been identified by Middlebrook et al. [1993] involving the freezing of SAT, indicating that addition of water during cooling a H_2SO_4 film more concentrated than 57.6 wt % promoted SAT formation.

Note that, although the present supercooling experiments suggest the probable freezing behavior of stratospheric aerosols, they do not provide definitely quantitative information. This is a consequence of the stochastic nature of the nucleation process. Indeed, the crystallization observed in ouJ" experiments may be duc to heterogeneous nucleation on the glass surfaces. *1* Ience, these observations yield only upper limits to the probable freezing temperatures, since the effects of glass surfaces and large sample sizes in our experiments increase the nucleation rate.

Melting of SAM

While the situation with respect to supercooling and freezing of sulfuric acid films may not be definitive, the melting of SAM can be reasonably defined, This is a process for which the equivalent of supercooling does not take place and hence its occurrence can be predicted reliably using laboratory results or based on thermodynamic. considerations.

The melting measurements were performed by first establishing a SAM film in the flow

tube. The substrate temperature was then slowly lowered while keeping a constant water partial pressure. Figure 3 displays a P_{H2O} versus $1/T$ phase diagram for the H_2SO_4/H_2O binary system, The experimental melting points obtained at different H_2O partial pressures are plotted as open circles. The stability regimes of various sulfuric acid hydrates are also indicated. The shaded area refers to the temperature and H_2O partial pressure conditions likely to be found in the stratosphere. It is evident in this figure that the melting point of the monohydrate depends primarily on the water partial pressure. Essentially, a cooling process at a constant H_2O partial pressure involves transformation of H_2O-rich to H_2SO_4-rich hydrates, accompanied by only a minor change in the bulk composition of the film. 'l'his was accomplished by admitting a small amount of H_2O into the system during cooling, The results show that the monohydrate melted upon cooling, that is, when the equilibrium composition was outside the SAM stability region, This implies the absence of a solid-solid phase transformation, i.e., the monohydrate did not transform into any of higher hydrates, but instead it melted at the temperature at which it was in equilibrium with a liquid solution having the same H_2O partial pressure, Nucleation of both di - and tri - hydrates of sulfuric acid has been known to be inefficient [Gable et al., 1950]. These observations are similar to the melting of SAT described previously by Middlebrook et al. [ ] 993] and Zhang et al. [1993] and in consistent with thermodynamic considerations of phase equilibria of the binary system [Wooldridge et al., 1994].

Heterogeneous Reactions

Reaction probabilities on SAM films were obtained from measurements of pseudo-first-order rate coefficients corresponding to the reactant loss. As a first approximation, the surface area of sulfuric acid films was assumed to be the geometric area of the flow tube; potential effects of surface roughness and porosities on the uptake coefficients will be addressed in the next section, The reaction probabilities were studied as a function of thermodynamic state of the substrate, which was adjusted by varying the temperature at a constant P_{H2O} or by varying P_{H2O} at a constant temperature,

N_2O_5 Hydrolysis. Figure 4 illustrates typical behavior of the N_2O_5 signal as a function of injector position on SAM. The experiment was performed at 210 K and at $P_{H2O} = 1 \times 10^{-4}$ Torr, equivalent

to a SAM surface of the H_2O-rich form. A N_2O_5 partial pressure of about 4x 10"7 Torr was used in the experiment. It is evident that the lost rate of N_2O_5 follows pseudo-first-order kinetics, with a reaction probability of *0.0026* calculated from the rate coefficient. Also shown in this figure for comparison is an experiment performed on a 70 wt% liquid sulfuric acid, yielding a reaction probability of 0.11. On liquid sulfuric acid, this reaction has been shown to be independent of the acid content [e.g., DeMore et al., 1992; Kolb et al., 1994]. The most distinctive feature in this figure is that even on the H_2O-rich SAM the observed uptake coefficient of N_2O_5 is about 50-fold slower than that found On liquid acid. This lower reactivity of frozen sulfuric acid may be explained by the nature of the reaction mechanism, which has been suggested to involve dissociation of N_2O_5 into NO_3^- and NO_2^+ ions [Mozurkewich and Calvert, 1988]: the occurrence of this dissociation may be suppressed upon freezing.

Figure 5 shows results of the uptake coefficients of N_2O_5 on SAM as a function of the H_2O partial pressure at 210 K. In these experiments, the N_2O_5 partial pressure was maintained in the range of (4-7) x10-7 Torr. The open and filled symbols denote the γ's measured using EIMS and Cl MS, respectively. in genera], the differences using these two detection schemes were negligible within the experimental uncertainty, although the uptake appeared to saturate rapidly using EIMS, owing to interference from 1 HNO_3 (both N_2O_5 and HNO_3 were detected at m/e = 46 corresponding to the NO_2^+ fragment ion in the EIMS). in the isothermal experiments, a readjustment of the H_2O partial pressure in the flow tube was followed by a corresponding change in the thermodynamic state (or in the composition) of the SAM film, occurring mostly on its surface layer [Molina, 1994]. Also, precautions were taken to avoid partial melting of the substrate, which could cause a greater uptake coefficient due to the presence of a small amount of liquid, It is clear in Figure 5 that the uptake coefficient of N_2O_5 on SAM exhibits a strong dependence on P_{H2O}: the value on the 1 H_2O-rich form is about 10"3, whereas it decreases by about an order of magnitude for the acid-rich form, This appears to reflect the reduced chemical potential of H_2O in H_2SO_4-rich surfaces: the tight H_2O bonding in the H_2SO_4-rich surfaces results in a lesser efficiency for N_2O_5 to bc hydrolyzed. A similar behavior has also been observed for the hydrolysis of $ClONO_2$ on nitric acid trihydrate [Abbatt and Molina, 1992] and on sulfuric acid tetrahydrate [Zhang et al., 1994b]. Additional results of the N_2O_5 uptake coefficients on SAM arc presented in '1'able I.

Temperature dependence of the uptake coefficients was evaluated by keeping a constant H_2O partial pressure and varying the temperature of the solid, a process also involving transformation of 1120-rich to H_2SO_4-rich hydrates as the substrate was heated from 190 to 225 K at a 1120 partial pressure (- 2x 10^{-5} l'err) in these experiments. These results are given in Figure 6, which plots γ as a function of temperature conducted at P_{N2O5} z-(4-7)x 10-7 Torr. As shown in this figure, there is a marked dependence of γ on temperature: at higher temperature (T > 220 K) the reaction probability was about 10-4, whereas the value approached 0.001 at temperatures near 200 K. Note that the H_2O partial pressure in these experiments was substantially smaller than that normally found in the stratosphere. This is because SAM would melt at much higher temperatures if higher P_{H2O} were applied, as discussed above.

The N_2O_5 hydrolysis on solid SAT substrates has been previously studied by Hanson and Ravishankara [1993]. Our results on 1 I_2O-rich SAM arc in general comparable with the reported values by these authors, but their measured γ's on SAT exhibited little variation with the thermodynamic state of the substrate (or relative humidity in their case).

$ClONO_2$ Hydrolysis. Reaction probability measurements for the $ClONO_2$ hydrolysis were conducted in the same manner as those for the N_2O_5 hydrolysis, Figure 7 presents the $ClONO_2$ signal as a function of injector distance for a SAM substrate at 210 K and a H_2O partial pressure of 1 x10"^{4}Torr. The reaction probability for this experiment corresponded to a value of ~ 2x1 0^{-4}. 1 .oss of $ClONO_2$ on SAM solid was in general very slow, even on the H_2O-rich form. Hence, this value is likely to be interpreted as the upper limit for this reaction on SAM, in addition, such a reaction probability would be consistent with that determined on H_2SO_4-rich SAT [Hanson and Ravishankara, 1993; Zhang et al., 1994b]. An experiment performed on a 65 wt °/₀ liquid is also shown in the figure for comparison, $ClONO_2$ hydrolysis on liquid sulfuric acid has been shown to depend on the acidic content [e.g., DeMore et al., 1992; Kolb et al., 1994; Zhang et al., 1994a].

$ClONO_2$ and N_2O_5 Reactions with 11(,'/. The reactive uptakes of $ClONO_2$ and N_2O_5 by SAM in the presence of HCl vapor were studied by first exposing the substrate with HCl vapor at the HCl partial pressure range of (2-8)x1 0^{-7}Torr. With /'$_{ClONO2}$ 'r P_{N2O5} in the range 'f (2,-8)X] 0-7 "err and temperatures between 200 and 220 K, there was no observable enhancement in the uptake coefficients over the corresponding hydrolysis values, nor any Cl_2 or $ClNO_2$ production. A

conservative upper limit of 1 0"[4] can be placed on both reactions. The very low uptake coefficients of these two reactions on SAh4 are perhaps not surprising, in light of lesser availability of HCl on the SAM surfaces, which has been real ized to depend on the water activity [Molina et al., 1993].

BET Surface A rea Measurements

A current outstanding issue of heterogeneous chemistry on solid substrates concerns surface roughness and porosities in laboratory simulations of PSCs. The work by Keyser et al. [1 991] and Keyser and Leu [1993] has demonstrated that ice and HNO_3-H_2O ice films prepared by vapor deposition can be porous, thus affecting reaction probability measurements. This effect is most pronounced for small γs where internal diffusion in a porous solid leads to a high number of collisions with the surface. 1 lere we report the first determination of surface areas and porosities of frozen sulfuric acid hydrates. BET surface areas were measured on SAM and SAT films formed in a manner similar to that used to produce the substrates for the flow tube experiments.

A typical Kr adsorption isotherm on crystalline SAM is shown in Figure 8 as a function of relative pressure, P/P_o, where P_o is the saturation vapor pressure of the adsorptive. Figure 8 shows that the isotherm is continuous without sharp changes below the saturation pressure; the shape is approximately classified as type II, which is often characterized as monolayer adsorption at low pressures followed by additional multi-layer adsorption with increasing pressures. The amount of Kr adsorbed is related to the surface area of the solid by the BET equation [e.g., Gregg and Sing, 1982],

$$P/[V(P_o - P)] = 1/(V_m C) + P(C - 1)/(V_m C P_o) \quad (7)$$

where J' is the adsorbed volume in units of cm^3 at STP, V_m is the monolayer capacity, and C is the BET constant. Hence a plot of $P/[V(P_o - P)]$ versus the relative pressure should be linear. The BET plot corresponding to the data displayed in Figure 8 is shown in Figure 9. The line through the data is a linear least-squares fit at the relative pressures between 0.05 and 0.4; a surface area of *0.0s4* $m^2 g^{-1}$ was inferred from the BET analysis for this particular case. The values for the saturation vapor pressure of Kr at liquid nitrogen temperature and its molecular area used in the

BET analysis were 1.70 Torr and 20.2 Å^2, respectively. Table II summarizes surface area measurements performed on SAM substrates. Several points should be noted in Table II. First, there is no appreciable correlation of the BET area with sample weight under identical experimental conditions. Second, in onc experiment, a sample was frozen at about 230 K and then was warmed to higher temperatures for about 30 min. No significant effect of annealing was observed on the surface area. The measured BET surface areas for SAM films were generally greater than the geometric area (45 cm^2) by a factor of about 5-10, indicating that crystalline SAh4 substrates arc moderately porous (which is also in consistent with the photography shown in Figure 1). These values, however, arc much lower than the BET areas of H_2O and HNO_3-H_2O ice films formed by vapor deposition [Keyser and Leu, 1993].

For comparison we also performed some experiments on SAT substrates: Figure 10 shows the adsorption isotherm for Kr on a SAT film. This isotherm is qualitatively similar to that for SAM, but the smaller amount of gas adsorbed is indicative of a lower surface area for SAT. The corresponding BET plot is presented in Figure 11, Results of the BET surface area measurements over SAT films arc also listed in '1'able II. As indicated in Table II, the BET surface areas for SAT films are nearly identical to (or only slightly higher than) the geometric area in the adsorption cell, suggesting that the SAT film is likely composed of non-porous crystals. Therefore, the morphology of crystalline SAT appears to be very different from that of crystalline SAM,

For porous solid in general, the interaction of pore diffusion and surface reaction must be considered in order to extract the true reaction probability, as described in detail by Keyser et al. [1991]. The present data reveal that the SAM films formed by freezing liquid sulfuric acid are porous to some extent. Hence, the usc of the geometric area, as presented in the proceeding section, results in an experimental γ which is an upper limit to the true reaction probability.

Stratospheric implications

The present results show systematically that concentrated sulfuric acid (> 75 wt %) freezes readily to form SAh4 under conditions characteristic of the stratosphere. Furthermore, once formed, SAM can be thermodynamically stable in the temperature range of 22.0-240 K and in the

water pal-(is] pressure range of (1 -4)x1 0"[4] Torr. Note that there arc some drawbacks on extrapolating the present freezing observations to the stratosphere because of the stochastic nature of the nucleation process. in the stratosphere, it is likely that the nucleation of SAM may rely on the presence of freezing nuclei.

The melting experiments predict that SAM melts at low temperatures under stratospheric conditions; the stability of SAM is determined by the temperature and water partial pressure. 1 lence, the regions where SAM may form and persist could be very restricted in the stratosphere, Apparently, warmth and dryness favor the formation of SAM. At a typical stratospheric water mixing ratio of 5 ppmv at 100 mb (corresponding to 16 km), for example, the possibility of SAM existing at temperatures below 220 K can be eliminated. Therefore, if formed, the monohydrate is most likely to be found at mid- and low latitudes, dependent on the temperature and water partial pressure.

The formation of sulfuric acid monohydrate may have important implications for the stratospheric chemistry. Our reaction probability measurements reveal that SAM surfaces are very non-reactive, in particular, the hydrolysis of N_2O_5 is significantly suppressed on SAM. "l'his reaction, one of the important heterogeneous reactions occurring on sulfate aerosols, has been known to occur efficiently on liquid sulfate aerosols, with the consequence of affecting the NO_x budget and promoting the release of active chlorine. The proposed SAM formation could terminate this reaction channel.

Conclusions

In this paper wc have reported freezing/melting points and heterogeneous chemistry of sulfur c acid monohydrate. By use of a fast flow reactor coupled to mass spectrometric detection, wc have investigated sulfuric acid films that simulate stratospheric sulfate aerosols, The results suggest the possible formation of sulfuric acid monohydrate and, consequently, very slow heterogeneous reactions on SAM.

The measurements of BET surface areas show that SAh4 films formed by freezing liquid solutions can be porous as arc H_2O or HNO_3-H_2O ice films formed by vapor deposition, albeit to a lesser extent. in contrast, the BET analysis indicates that SAT films are likely composed of

non-porous crystals. This finding justifies earlier laboratory studies in which exterior or geometric surface areas were utilized when deducing reaction probabilities on SAT [Hanson and Ravishankara, 1993; Zhang et al., 1994b].

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Table 1. Uptake Coefficients of the **1** lydrolysis of N_2O_5 on SAM[a]

T (K)	P_{H2O} (Torr)	P_{N2O5} ('I'err)	
2.30	$3.6x10^{-4}$	4.7 X10"[7]	**7.5 X10-4**
230	2.8 X10-4	$5.2x10^{-7}$	$5.9x10^{-4}$
230	$2.1x10^{-4}$	$6.0x10^{-7}$	**$5.2x10^{-4}$**
220	$2.1x10^{-4}$	$5.2x10^{-7}$	**9.1 XI O-4**
220	$1.5x10^{-4}$	S,3X10-[7]	$8.5x10^{-4}$
215	$1.1x10^{-4}$	$5.6x10^{-7}$	$1.1x10^{-3}$

[a] Data obtained using CIMS.

"1'able 11. BET Sul-face Areas of crystalline H_2SO_4 Hydrates[a]

Substrate	Weight (g)	Monolayer[b] (μmoles g-')	BET constant	Surface area[b] ($m^2 g^{-1}$)
SAM	0.592.	**0,422**	**48.8**	0.051
SAM	0.40s	**0.444**	**79.3**	0.054
SAM	0.596	**0.331**	**64.8**	0.040
SAM[c]	0.685	**0.306**	**82.2**	0 . 0 3 7
SAM	1.120	**0.3s3**	**58.7**	0.043
				av = 0.04S ±1 0.0073 (1σ)
SAT	0.188	*0.215*	**24.6**	0.026
SAT	0.324	0.186	**22..8**	0.023
				av = 0.025:1 0.0022 (1σ)

[a] Adsorbate gas was Kr and the crystalline hydrates were made from freezing liquid solutions; geometric area of the sulfuric. acid films was *45* cm^2.

[b] Sulfuric acid surface area was obtained by subtracting the cold Pyrex surface area in the adsorption cell, ~ 145 cm^2.

[c] Sample was annealed to 273 K for about 30 min after freezing.

Figure Captions

Figure 1. A crystalline SAM film formed in the flow tube by freezing liquid solutions at 220 K. See text for details.

Figure 2. Freezing temperatures of various H_2SO_4 solutions studied in the flow tube/mass spectrometer apparatus. Weight percents at the freezing points (open triangle) were calculated from the temperature and 1 I_2O vapor pressure, based cm 1 I_2O vapor pressure data of the H_2SO_4/H_2O solutions from Zeleznik [1 991] and Zhang et al. [1993]. Also shown in this figure is the freezing envelop of sulfuric. acid [Gable et al., 1950]. The horizontal bar denotes the composition range over which the films were held at temperatures below 190 K without freezing. The dotted line a-b corresponds to the extension of the coexistence line between liquid and SAM. The smooth dashed curves represent equilibrium sulfuric acid compositions of stratospheric aerosols at H_2O mixing ratios of 5.0, 3.0, and 1.5 ppmv at 100 mb (corresponding to about 16 km).

Figure 3. Observed melting temperatures (open circles) of sulfuric acid monohydrate (SAM) plotted in a P_{H2O} versus $1000/T$ phase diagram [Zeleznik, 1991; Zhang et al., 1993]. The shaded area corresponds to temperature and H_2O partial pressure conditions likely to be found in the mid- and low latitude stratosphere. The dotted line a-b is as in Figure 2. The data show that SAM can be thermodynamically stable in the temperature range of 220-240 K and in the water partial pressure range of (1 -4)x1 0^{-4} Torr anti that SAh4 melts when the temperature and equilibrium H_2O vapor pressure arc outside of its stability regime.

Figure 4. N_2O_5 signals as a function of injector position for an experiment performed on a SAM film at 210 K and $P_{H2O} \approx$ lx] 0^{-4} Torr (solid line, solid circles). Also shown for comparison is an experiment on a 70 wt % H_2SO_4 liquid film at 218 K (dashed line, open circles). Both experiments were carried out using CIMS. Experimental conditions: $P_{N2O5} =$ 4x1 0^{-7} '1'err, $P_{He} =$ 0.4 "1'err, and flow velocity $\approx$ 1800 cm S-l.

Figure 5. Reaction probability of N_2O_5 with H_2O as a function of P_{H2O} on SAM surfaces at 210 K. The open and filled symbols refer to measurements using EIMS and

CIMS, respectively. Experimental conditions: P_{N2O5} = (4-7)x1 0^{-7} '1'err, P_{He} = *0.4* to 0.5 ']'err, flow velocity = 810 to 1800 cm S-l, and T = 210 K,

Figure 6. Reaction probability of N_2O_5 with 11_20 as a function of temperature on SAM surfaces. The open and filled symbols refer to measurements using EIMS and CIMS, respectively. Experimental conditions: P_{N2O5} = (4-7)x 10-7 Torr, P_{He} = 0.4 to 0.5 "1'err, velocity = 810 to 1800 cm s^{-1}, and P_{H2O} = 2X10-S Torr.

Figure *7.* $ClONO_2$ signals as a function of injector position for experiments performed on a SAM film at 210 K and $P_{H2O} \approx$ 1x10"^{4} Torr (solid line, filled circles) and on a 65 wt % liquid H_2SO_4 film at 212 K. Both experiments were carried out using CIMS. Experimental conditions: $P_{ClONO2} \approx$ 4x1 0"^{7} l'err, P_{He} = 0.4 Torr, and flow velocity $\approx$ 1800 cm s^{-1}.

Figure *8.* Adsorption isotherm of Kr on 0.405 g of crystalline SAM (84.5 wt %) at 77.5 K.

Figure *9.* BET plot of $P/V(P_o - P)$ against P/P_o for the data displayed in Figure 8.

Figure 10. Adsorption isotherm of Kr on 0.188 g of crystalline SAT (57.6 wt %) at 77.5 K.

Figure 11. Same as Figure 9 except for the data displayed in Figure 10.

14 mm

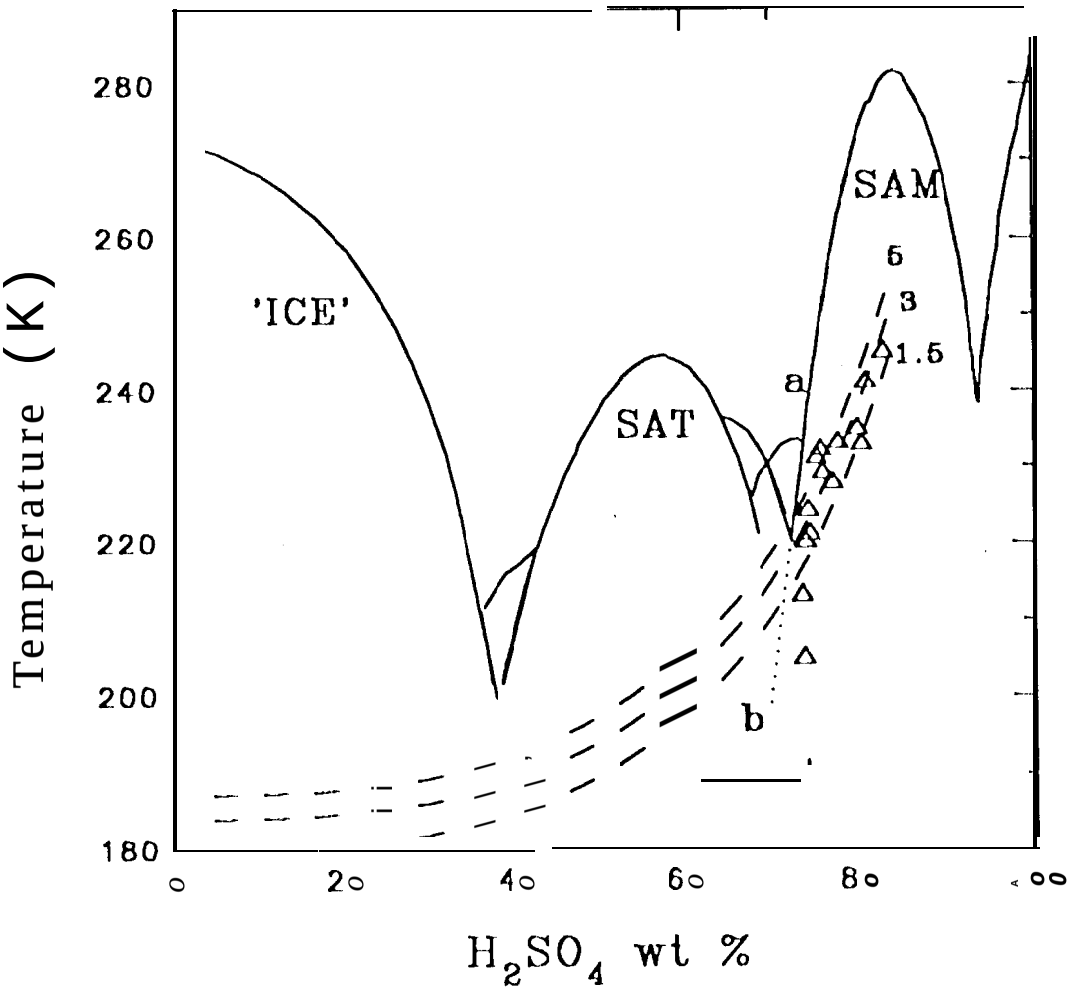

280
260
240
220
200
180
Temperature (K)
'ICE'
SAT
SAM
5
3
1.5
a
b
0
20
40
60
80
100
H_2SO_4 wt %

Fig.

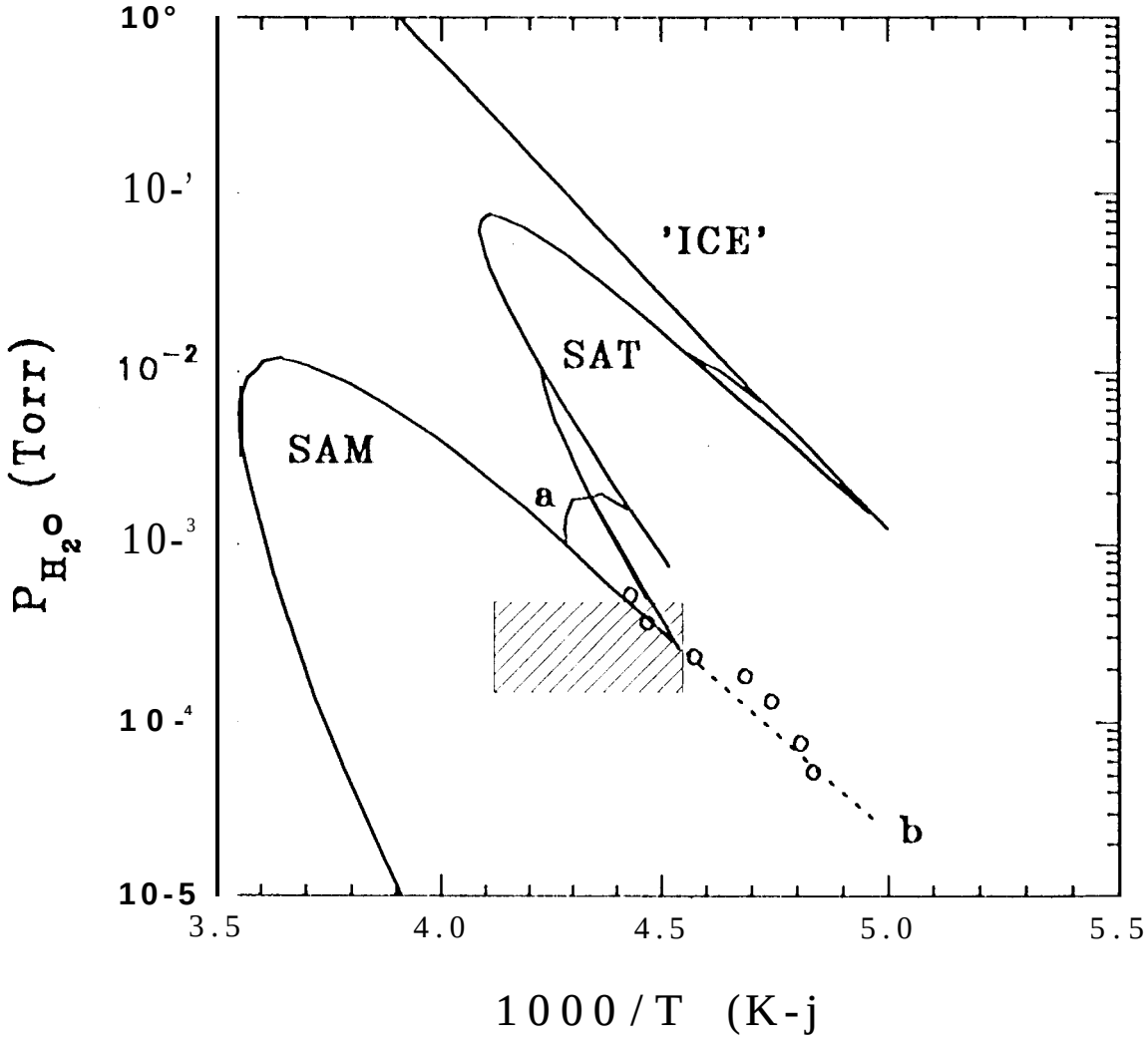
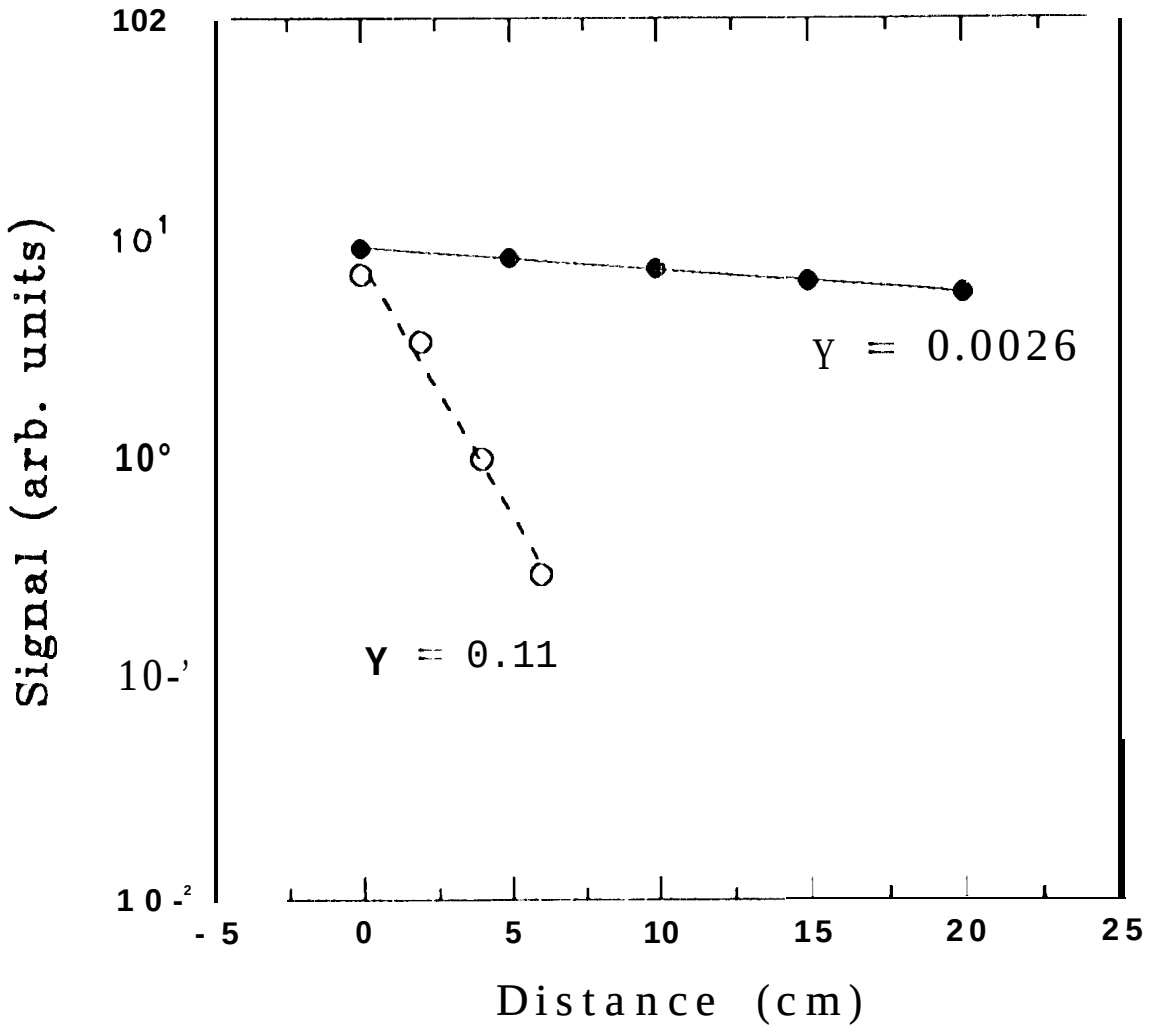
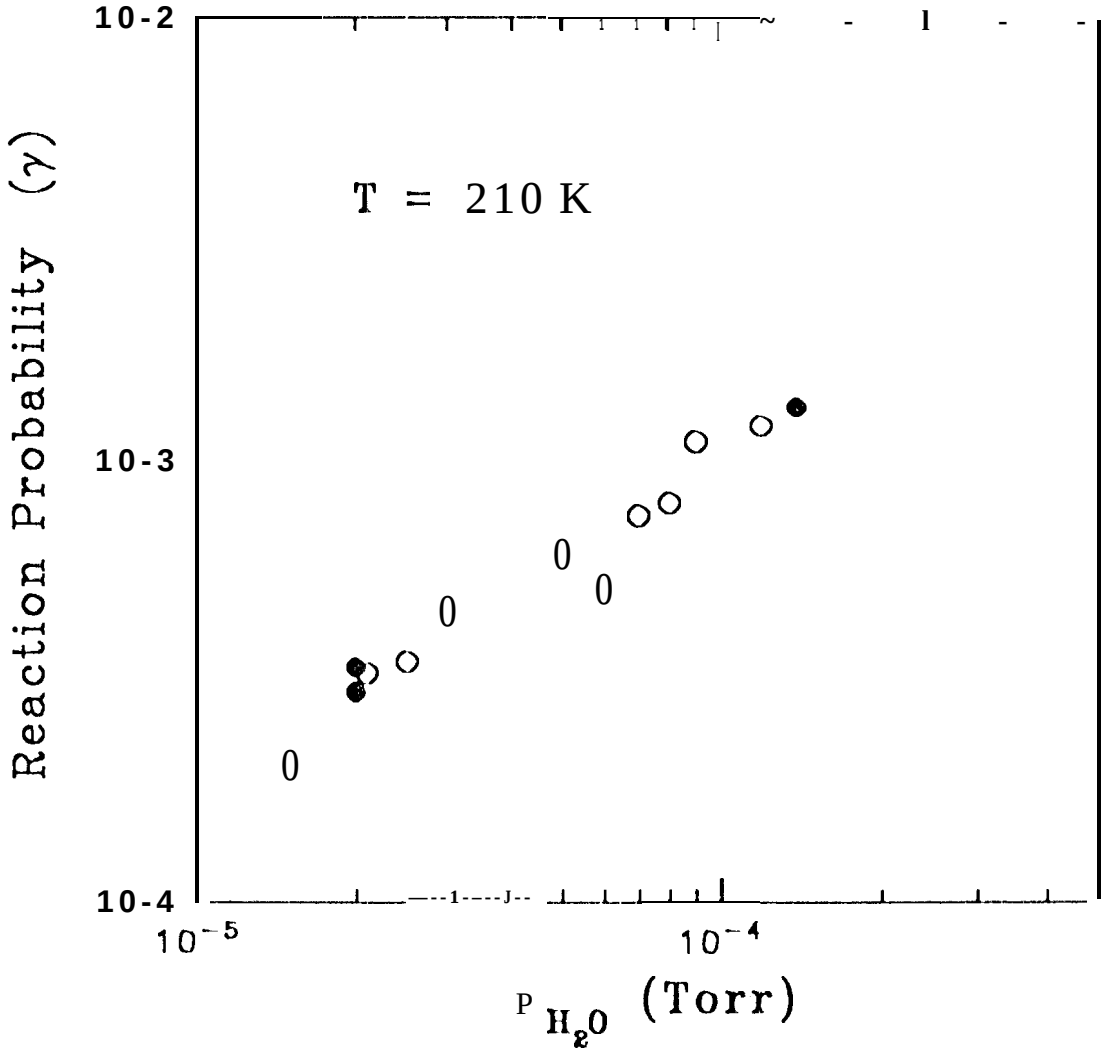

10°
10-'
10-2
10-3
10-4
10-5
P_{H_2O} (Torr)
'ICE'
SAT
SAM
a
b
3.5
4.0
4.5
5.0
5.5
1000/T (K-j

Fig 3


102
10¹
10°
10-'
10-²
Signal (arb. units)
Y = 0.0026
Y = 0.11
- 5
0
5
10
15
20
25
Distance (cm)



F-35

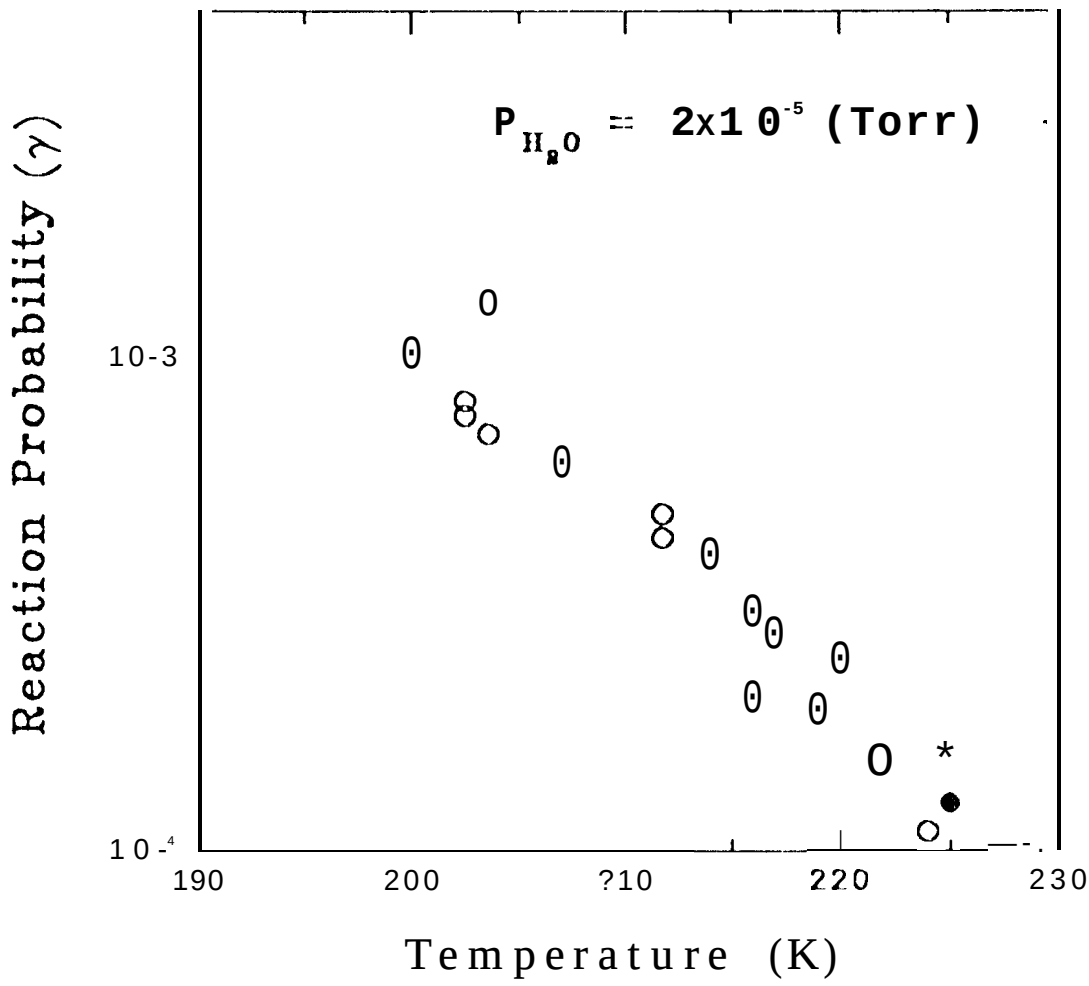
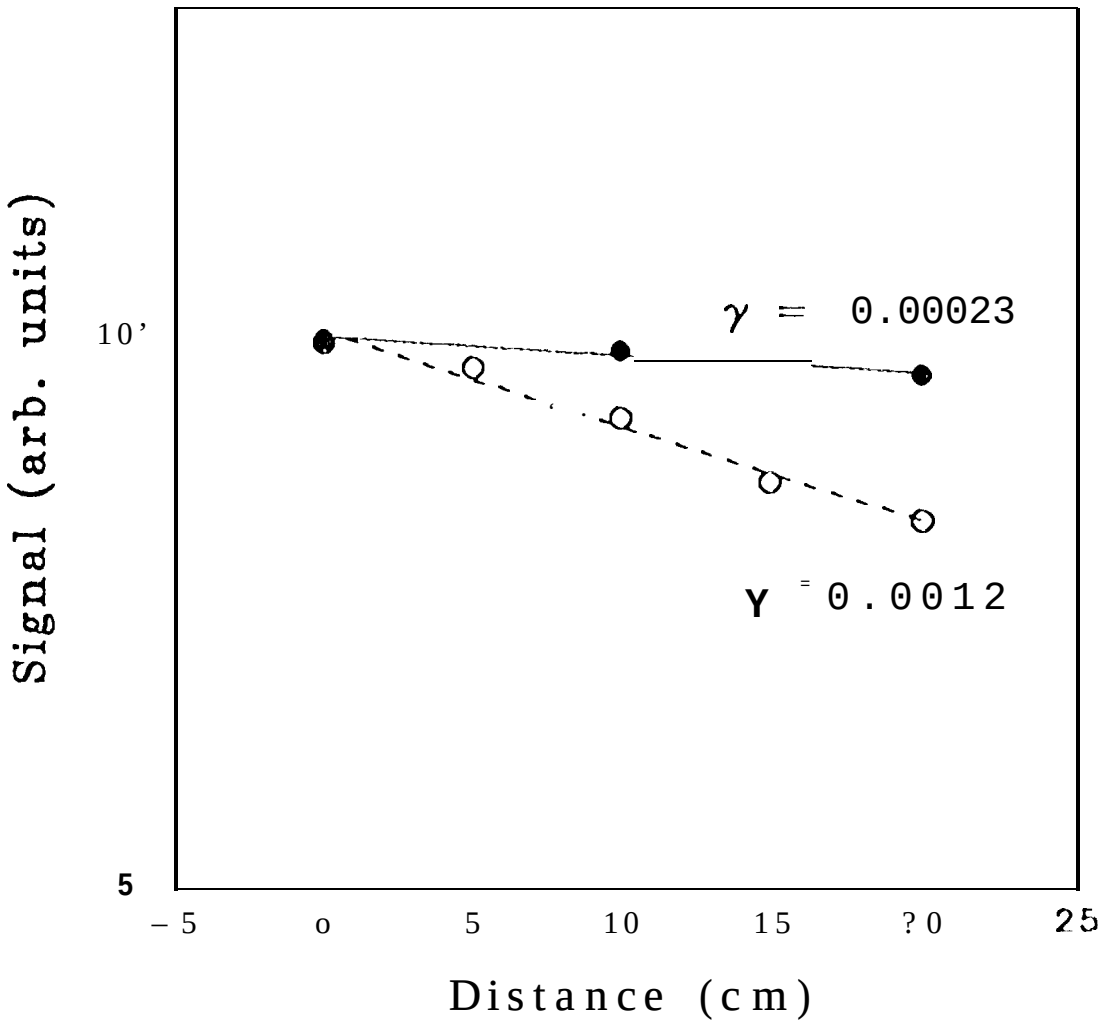
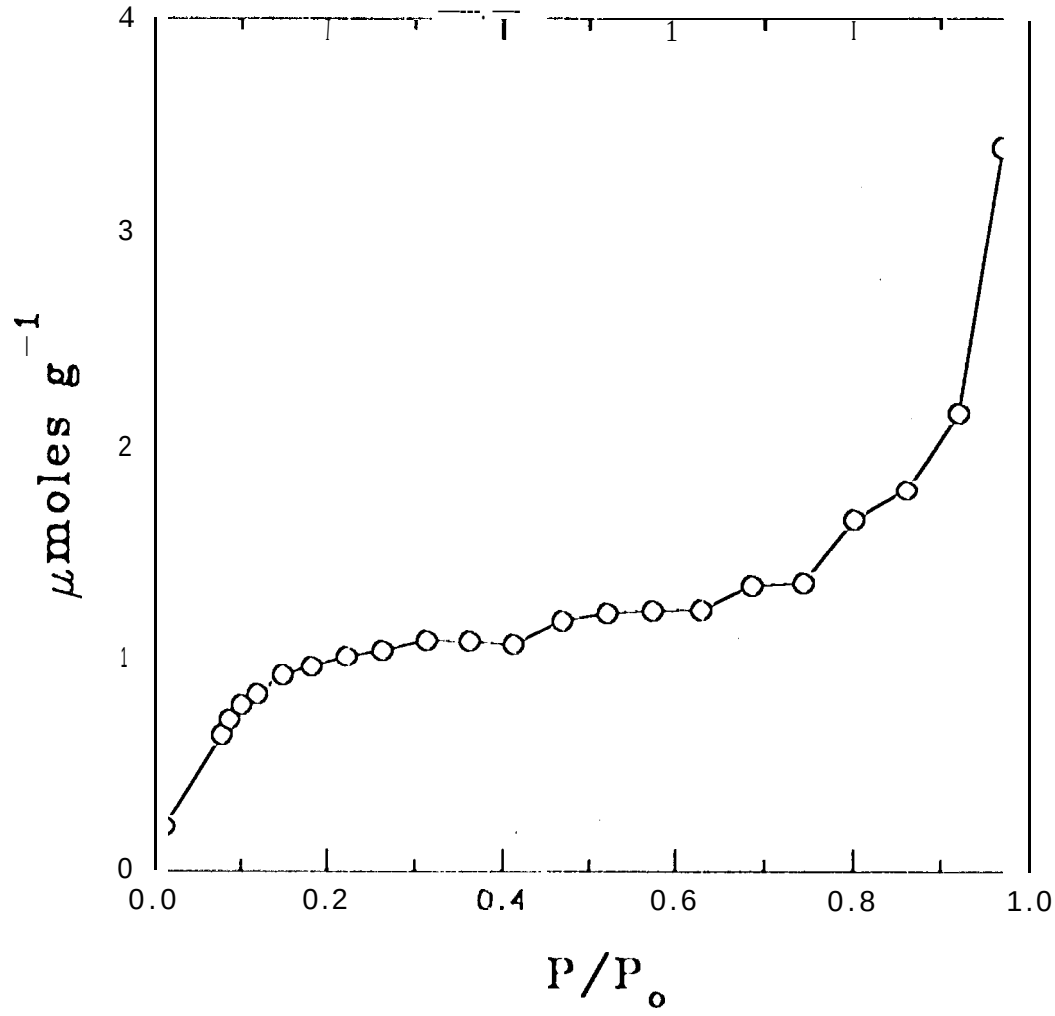
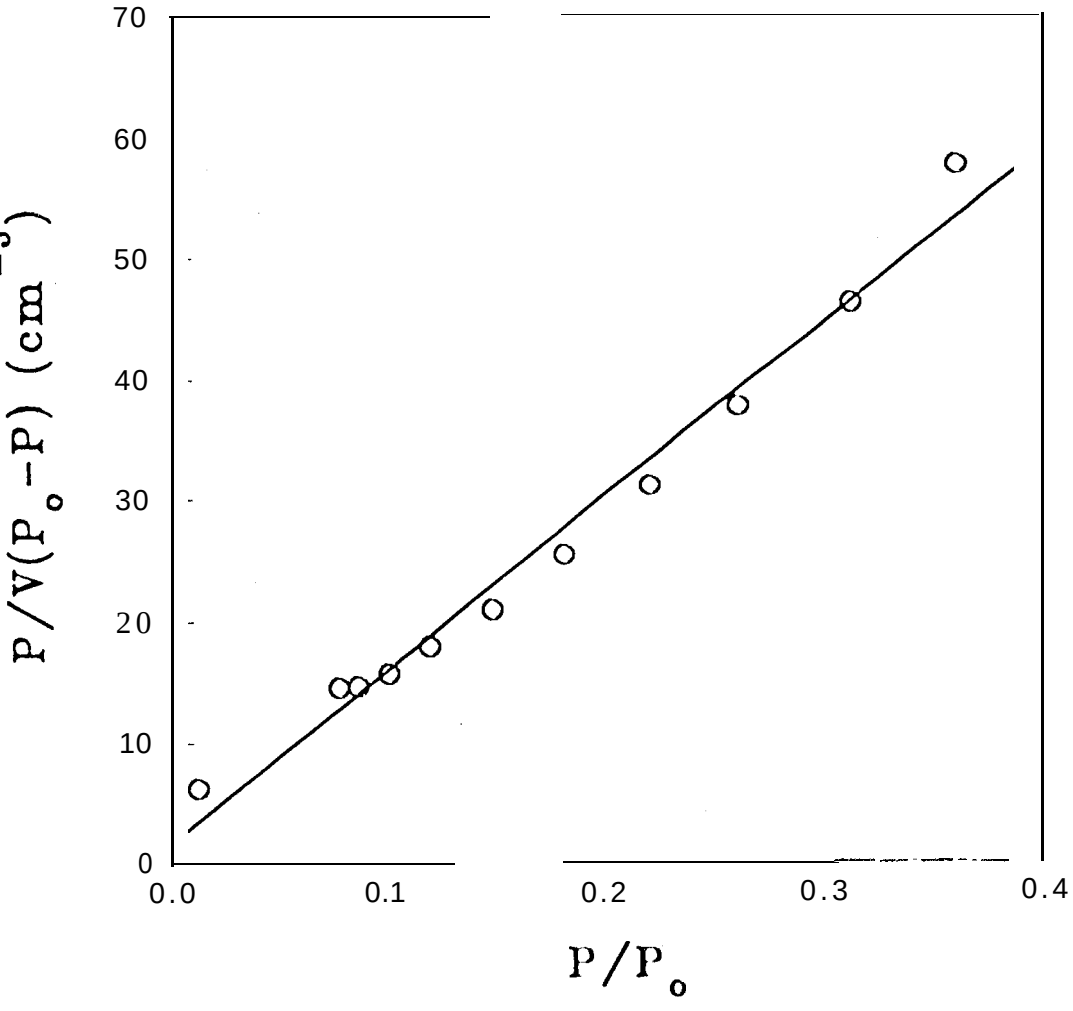

P_{H_2O} = 2x10^{-5} (Torr)
Reaction Probability (γ)
10-3
10-4
190
200
?10
220
230
Temperature (K)

Fig 6


Signal (arb. units)
10'
5
γ = 0.00023
Y = 0.0012
– 5
o
5
10
15
?0
25
Distance (cm)


4
3
2
1
0
μmoles g⁻¹
0.0
0.2
0.4
0.6
0.8
1.0
P/P₀



F-29

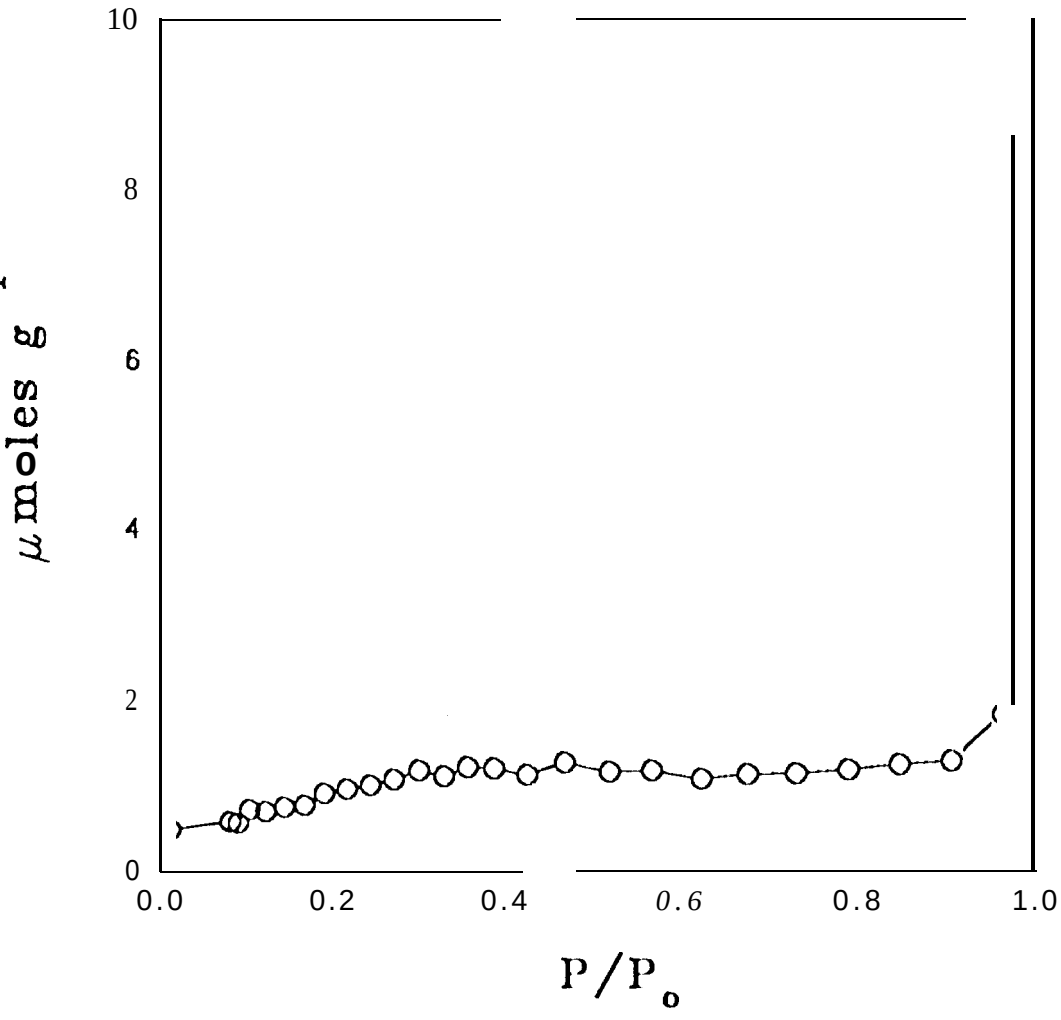
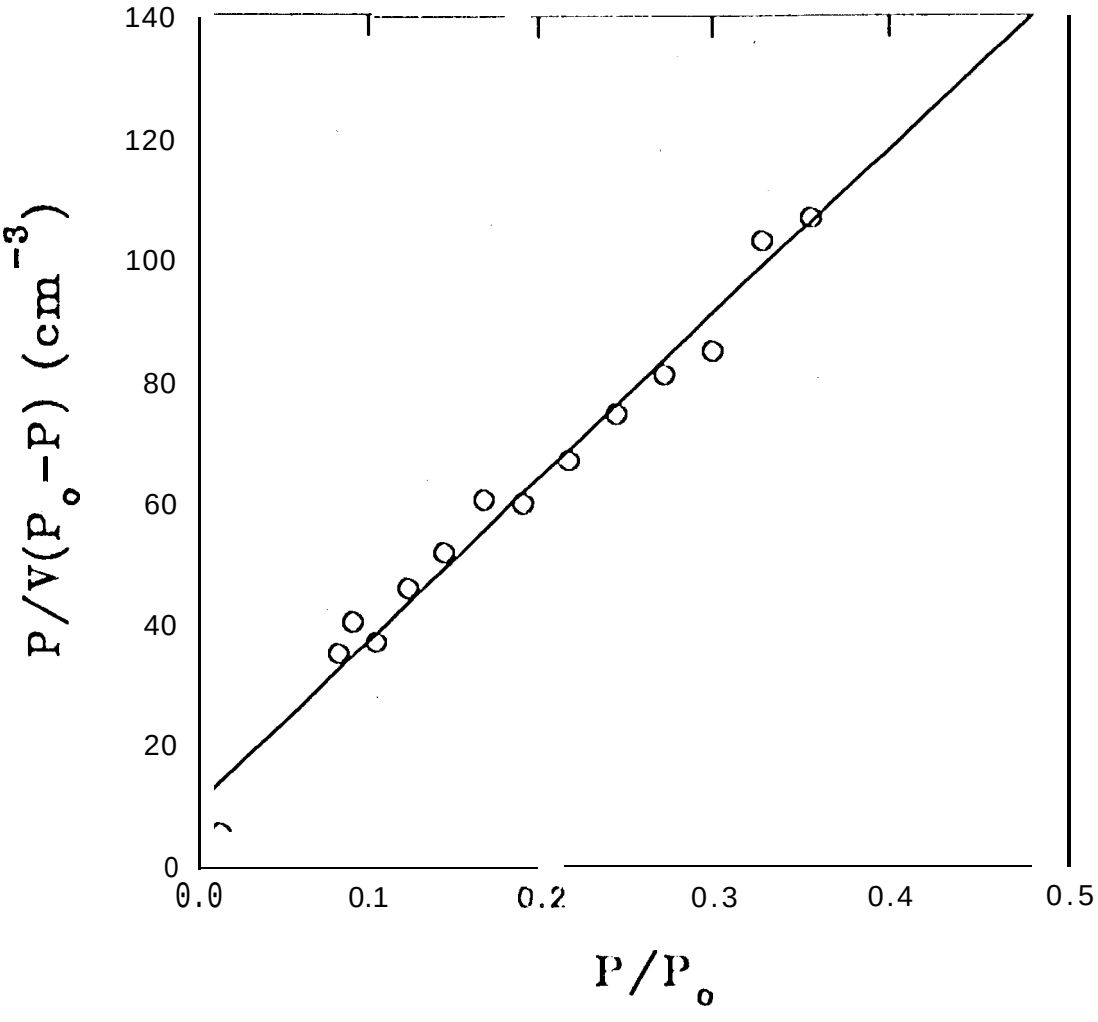


Fig. 10


140
120
100
80
60
40
20
0
0.0
0.1
0.2
0.3
0.4
0.5
P/V(P$_o$-P) (cm^{-3})
P/P$_o$